Calculation of the breakthrough time of an organic substance through a fixed layer of active carbon

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The results of investigations of the adsorption dynamics of organic substances on active carbons (AC) moistened to equilibrium over a wide range of breakthrough concentrations are discussed. The features of adsorption dynamics typical for the moisture-free AC in the region of low breakthrough concentrations are also present when they are moistened to equilibrium. The equations for calculating the breakthrough time of low concentrations through a fixed layer of equilibrium moistened AC corresponding to the maximum permissible concentrations are derived.

Key words: active carbon, adsorption; porous structure, breakthrough time.

The adsorption method using microporous adsorbents is the most effective and prevalent technique for purifying the industrial waste gases containing vapors of from 40 to 130 harmful organic compounds.[1] Therefore, the study of the regularities of adsorption dynamics is of great significance, particularly in the region of relatively low breakthrough concentrations corresponding to the maximum permissible concentrations (MPC) of harmful substances. The regularities of the dynamics of the adsorption of benzene vapor on moisture-free AC in the region of low breakthrough concentrations have been considered previously.[1-5] A mathematical approach has been developed and an equation for calculating the breakthrough time of substances through a fixed layer of sorbent has been suggested.

The presence of moisture in the air and in AC increases the efficiency of these purification processes.[6-8] Consequently, studying the regularities of the dynamics of the adsorption of vapors of organic substances on moistened AC is of extreme importance.

This work is devoted to an investigation of the adsorption dynamics of vapors of organic substances on AC in the presence of water over a wide range of breakthrough concentrations, to a study of the regularities of adsorption dynamics in the region of relatively low breakthrough concentrations of deleterious organic substances, and to the development of a mathematical approach to calculating the breakthrough time for low concentrations corresponding to MPC through a fixed layer of AC.

Experimental

The adsorption dynamics of vapors of the organic substances were investigated on the active carbon AC-1, whose porous structure consists of micro-, supermicro-, meso-, and macropores. In some experiments other AC's were used. The characteristics of the porous structure of AC's under investigation are presented in Table 1.

Organic compounds with various geometric and electronic structures, hexane, cyclohexane, benzene, perfluorobenzene, dioxane, and tetrachloromethane, were chosen as the adsorbates. A study of the joint adsorption of organic substances and water vapor was carried out by the previously[2] described procedure, allowing individual output curves to be obtained for each component of the mixture.

Practically dry air as well as air with different relative amounts of moisture (up to 90 %) was used. The sorbents were preliminarily moistened by water vapor at a fixed humidity (φ) to equilibrium ($W_{eq} = \varphi$). Adsorption of the organic substances was carried out at the same humidity as pre-adsorption

Table 1. Characteristics of the porous structure of active carbons

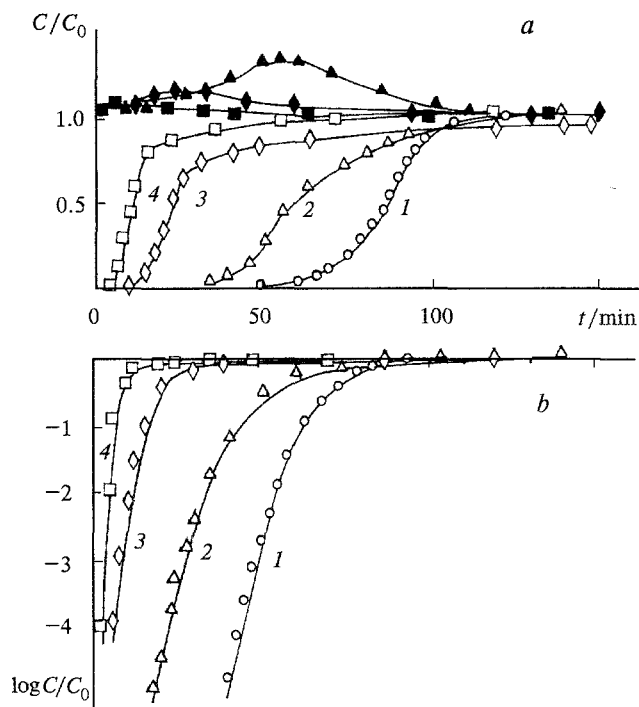| Adsorbent	W_{01} /cm^3 g^{-1}	E_{01} /kJ mol^{-1}	W_{02} /cm^3 g^{-1}	E_{02} /kJ mol^{-1}	V_{meso} /cm^3 g^{-1}
AC-1	0.214	22.73	0.056	9.50	0.120
AC-2	0.236	24.32	—	—	0.110
AC-3	0.489	28.00	—	—	0.022

Fig. 1. Output curves of the joint adsorption of cyclohexane and water (*a*) and the initial sections of the curves in semilogarithmic coordinates for cyclohexane (*b*) on equilibrium moistened active carbon AC-1 (L = 20 mm) at varios humidities, $\varphi = W_{eq}$ (%): 0 (*1*), 40 (*2*), 65 (*3*), and 75 (*4*). Dark dots correspond to displacement of water.

of water. The concentrations of the substances in the gas—vapor mixture, the specific rate, and the temperature were constant and equal to 3.8 mg L^{-1}, 0.5 L min^{-1} cm^{-2}, and 293 K, respectively. The experiments were carried out on adsorbent layers of various lengths (10, 20, 40, and 60 mm).

Results and Discussion

The output curves of adsorption on moisture-free AC as well as on AC moistened to equilibrium for the substances under consideration in a wide range of breakthrough concentrations were plotted according to the developed procedure. Figure 1 shows the output curves of cyclohexane adsorption on AC-1 at various relative humidities of the gas—vapor mixture and with equilibrium moistening of the adsorbent. Figure 2 presents the output curves of the adsorption of cyclohexane and benzene in the region of breakthrough concentrations on AC-1 for various lengths of the adsorbent layer; equilibrium moistening of AC and relative humidity equal 75 %.

A study of the dynamics of the adsorption of the organic substances by the layer of equilibrium moistened AC from a flow of moist air (see Figs. 1 and 2) showed that in the region of relatively low breakthrough concentrations a number of regularities can be seen. First, the
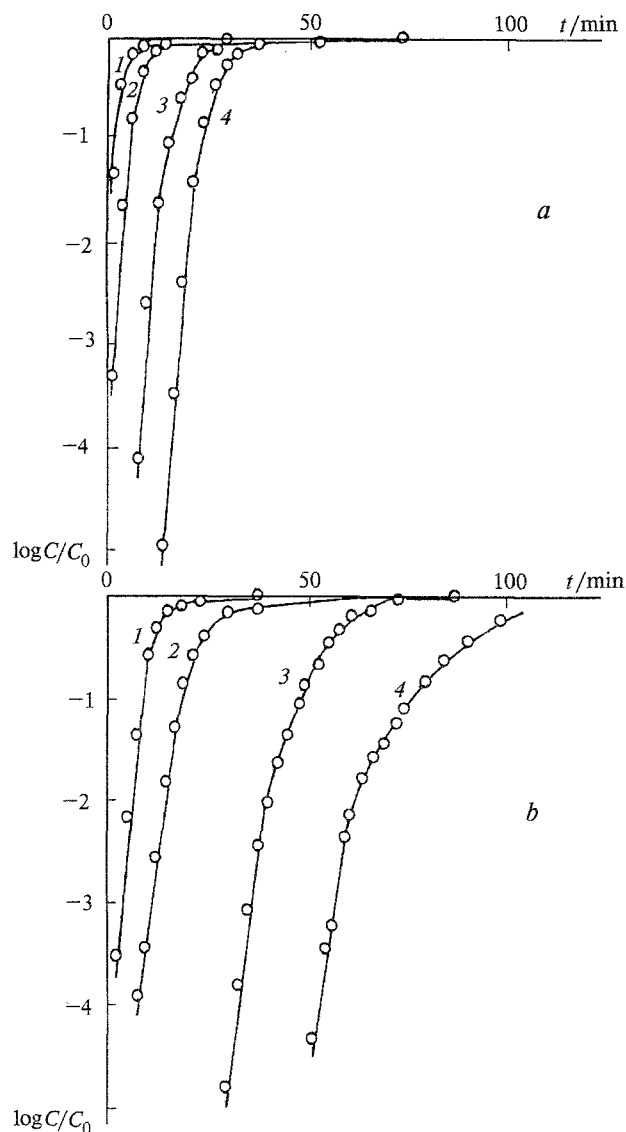

Fig. 2. Output curves of cyclohexane (*a*) and benzene (*b*) adsorption on equilibrium moistened active carbon AC-1 ($\varphi = W_{eq}$ = 75 %) for various lengths of the sorbent layer, L/mm: 10 (*1*), 20 (*2*), 40 (*3*), and 60 (*4*).

initial portions of the output curves are straight lines. The range of relative concentrations in which the linearity of the initial portions is observed for the adsorbed substances examined extends from 10^{-5} to 10^{-2}.

Second, for these substances there is a parallel shift of the linear portion of the output adsorption curves as the length of the equilibrium moistened layer changes (see Fig. 2). The parallelism of the linear portions is evidence that the fronts of low vapor concentrations move along the length of the adsorption layer at equal rates. This is clearly demonstrated in the plots of the isopycnic curves of adsorption (Fig. 3).

Third, as can be seen from Fig. 3, the formation of the region of relatively low breakthrough concentrations
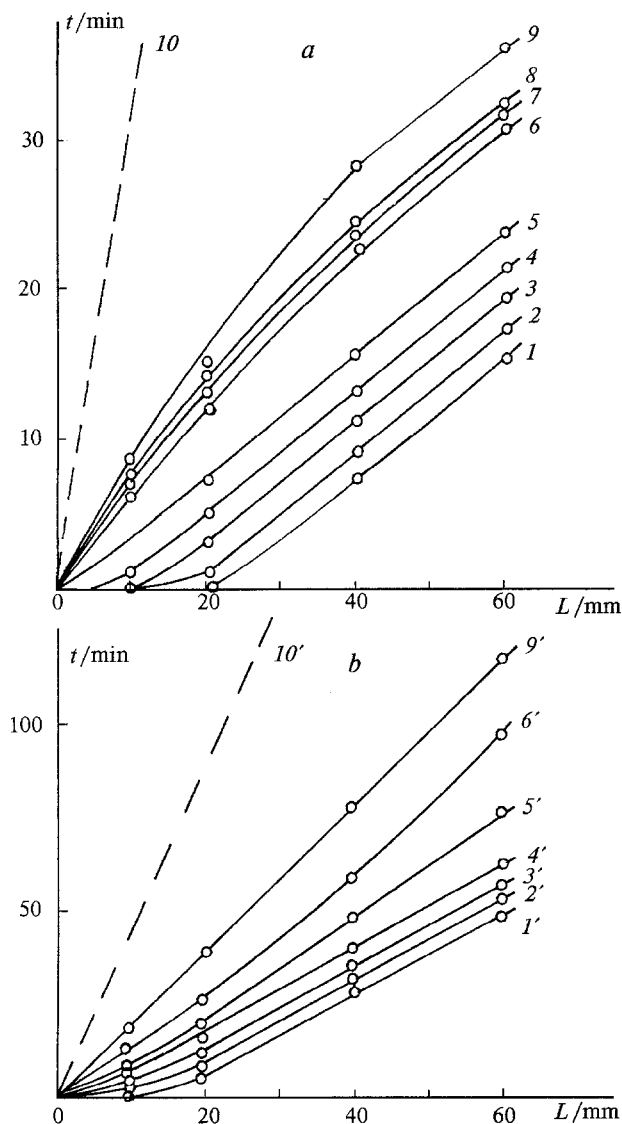
Fig. 3. Isopycnic curves of cyclohexane (*a*) and benzene (*b*) adsorption on moisture-free AC-1 and on AC-1 equilibrium moistened at $\varphi = W_{eq} = 75$ % at various relative concentrations: $C/C_0 = 10^{-5}$ (*1, 1'*); 10^{-4} (*2, 2'*); 10^{-3} (*3, 3'*); 10^{-2} (*4, 4'*); 10^{-1} (*5, 5'*); 0.5 (*6, 6'*); 0.6 (*7*); 0.7 (*8*); 0.9 (*9, 9'*), and 0.5 at $\varphi = W_{eq} = 0$ % (*10, 10'*).

for equilibrium moistened AC occurs in a relatively short time. This is followed by movement along the layer. For an AC layer of length <20 mm the region of low breakthrough concentrations is characterized by the presence of a nonstationary stage in the adsorption dynamics (the curve of the concentration distribution is deformed), whose duration is determined by the length of the working layer (for cyclohexane and benzene it is about 20 mm). In the region of layer length >20 mm the distribution curve of low concentrations begins to shift with a nearly constant rate (isopycnic curves are

parallel). The range of relative concentrations (C/C_0) in which the isopycnic curves are parallel is 10^{-5}—10^{-2} for cyclohexane and benzene.

This shape of output curves and isopycnic curves of adsorption in the region of low concentrations was also observed for moisture-free AC.[1—5] The isopycnic curves of cyclohexane and benzene adsorption at their breakthrough concentration, which is $0.5C_0$ on moisture-free AC, are presented for comparison in Fig. 3. The rate at which the vapors move along a layer is known[1—5] to be approximately equal to the rate of movement of a front of relatively low breakthrough concentrations. It is seen that although the character of the adsorption of these organic substances on moisture-free and equilibrium moistened AC are closely allied, the rate of movement of the adsorption front for equilibrium moistened AC is considerably greater than that for the moisture-free sorbent. In the case of higher concentrations ($C/C_0 > 10^{-2}$) the adsorption fronts of equilibrium moistened AC are subjected to substantial deformation. From the consideration of the isopycnic curves of adsorption it follows that the rates of movement of the adsorbed substances at these concentrations are considerably lower than in the region of low concentrations. This is particularly characteristic of benzene when AC layer length is >20 mm. The results obtained (see Fig. 1) indicate that when the breakthrough concentrations of the organic substances C/C_0 are $>10^{-1}$, intense displacement of water from the adsorption volume of the micropores is observed. The lower rate of movement of substances along a layer at these concentrations appears to be associated with the final rate of the mass exchange processes: the loss of moisture in part of the micropore volume, and slow diffusion and filling of the freed micropore volume with organic compounds through the action of the counter flow of the desorbed water molecules.

As the requirements for the quality of the purification of waste gases from vapors of harmful organic substances become stricter the determination of the breakthrough time of MPC of these substances through a fixed layer becomes a meaningful goal. Investigations have shown that for practically moisture-free and equilibrium moistened AC the breakthrough time (*t*) of MPC of organic substances through an adsorbent layer may be found from the equation describing the initial section in the region of relatively low breakthrough concentrations:

$$\log(C/C_0) = k + F't, \tag{1}$$

where *k* is the segment obtained by the intersection of the extension of the linear portion of the output curve and the *y* axis at an infinitely short time ($t \to 0$), or log (C'/C_0); C_0 is the initial concentration of the organic substance; C' is the breakthrough concentration when $t \to 0$; F' is the tangent of the slope of the linear section extended to the *x* axis. The *k* fragment or log (C'/C_0)

may be found from the equation for the effective kinetic coefficient of mass exchange[7] for equilibrium moistened AC:

$$\log(C'/C_0) = -[0.434(L/v) \cdot \beta_{eff}(1-\xi \cdot \theta_{H_2O})], \qquad (2)$$

where

$$\xi = (W_0/V_{meso})\exp[(2.3RT/E_0)^2 \cdot (R^*/R_H^*)-\psi/2],$$

L is the length of AC layer; v — linear rate of the gas-vapor mixture; β_{eff} — effective kinetic coefficient of mass exchange for practically moisture-free AC; θ_{H_2O} — water space factor of the adsorption space of AC micropores; W_0 — limiting volume of adsorption space of AC micropores; V_{meso} — volume of AC mesopores; R — gas constant; T — temperature; E_0 — characteristic adsorption energy of the standard vapor—benzene mixture; R^* — refraction of the examined organic substance; R_H^* — refraction of a H atom; ψ — total number of C atoms in the molecule and unpaired electrons for Cl, O, N, and other atoms.

The analysis of the data on the adsorption dynamics of organic substances in the region of relatively low breakthrough concentrations (see Fig. 1) showed that as the relative humidity and accordingly the amount of preliminarily sorbed water increase, the slope of the linear section of the output curve extended to the x axis changes for all organic substances under investigation. We believed that this is associated with a change in the equilibrium adsorption of the organic substance as the relative humidity and AC moisture content increase. From the experimental output curves of the adsorption dynamics, the equilibrium values of the adsorption of the examined substances on moisture-free AC and on AC moistened to equilibrium at different relative humidities were estimated.

Figure 4, a presents the dependences of the tangents of slopes (F') of the lines on the equilibrium adsorption
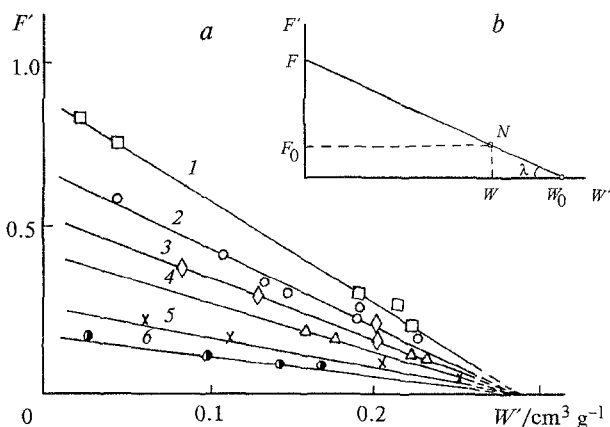

Fig. 4. *a.* Dependences of tangents of the slopes of the linear portions of the output curves on the equilibrium adsorption values occuring in dynamic experiments for hexane (*1*), cyclohexane (*2*), benzene (*3*), dioxane (*4*), perfluorobenzene (*5*), and tetrachloromethane (*6*).

b. Scheme of the determination of the tangent of slope (*F'*).

Table 2. Calculated (t_{calc}) and experimental (t_{exp}) values of breakthrough time through an AC layer for relative concentration $C/C_0 = 1 \cdot 10^{-3}$ ($L = 20$ mm, $v = 0.083$ m s^{-1}, $\phi = W_{eq} = 75$ %, $C_0 = 3.8$ mg L^{-1})

Adsorbent	Adsorbat	t_{calc}/min	t_{exp}/min
AC-1	Hexane	5.0	6.0
	Cyclohexane	3.0	4.0
	Benzene	10.8	11.0
	Perfluorobenzene	15.0	18.0
	Dioxane	27.0	30.0
	Tetrochloromethane	4.4	3.5
AC-2	Hexane	2.7	2.0
	Cyclohexane	1.0	0.5
AC-3	Hexane	0.0	0.0

values of the organic substance (W') occurring in dynamic experiments at various relative humidities and various equilibrium moistening of AC. The adsorption values are expressed in volume units, and the densities of the vapors of the organic substances are taken to be equal to the densities of the liquids at 293 K. As can be seen from Fig. 4, a, the tangent of the slope of the linear portion of the output curve increases as the relative humidity and amount of water adsorbed by AC increase. For all substances under investigation the dependence of the tangent of the slope on equilibrium adsorption are linear over the range of moistures considered, from moisture-free samples and air to those equilibrium moistened at $\phi = 90$ %. As this takes place for all of the substances examined, the straight lines intersect at the point on the x axis, whose value corresponds to the limiting volume of the adsorption space of the investigated AC micropores (W_0). The linear dependence of F' on W' (see Fig. 4, b) may be approximated by the following equation:

$$F' = F(1 - W'/W_0). \qquad (3)$$

To find the value of segment F let us consider Fig. 4, b. The point N with coordinates (W, F_0) is an experimental value of equilibrium adsorption, *i.e.*, it is tangent of the slope of the linear portion of the output curve of the adsorption of an organic substance for practically moisture-free AC. The ratio F/W_0 equals $F_0(W_0 - W)$, because the triangles have the common angle λ. Then

$$F = W_0 F_0/(W_0 - W). \qquad (4)$$

When the air and the AC layer are moisture-free the tangent of the slope of the linear portion of the output curve extended to the x axis may be found as follows:[1—5]

$$F_0 = 0.434 C_0 \beta_{eff}/(\alpha a), \qquad (5)$$

where a is the equilibrium adsorption of the organic substance on moisture-free AC; α is a coefficient that

takes into account the discrepancy between the t value obtained by extension of the linear portion of the output curve in the region of relatively low breakthrough concentrations until it intersects the x axis, and the output time of the half breakthrough concentration ($0.5C_0$). Substituting expression (5) in Eq. (4), and then (4) in Eq. (3), thereupon (3) and (2) in Eq. (1), the following expression for the calculation of breakthrough times of relatively low concentrations corresponding to MPC can be obtained after the necessary rearrangements:

$$t = [\alpha a/(C_0 v)] \cdot [(W_0 - W')/(W_0 - W)] \times$$
$$\times [(1 - \xi\theta_{H_2O})L - (2.3v/\beta_{eff})\log(C_0/C)]. \tag{6}$$

A comparison of the experimental and calculated values of the MPC breakthrough time for a number of organic substances and AC showed (Table 2) that Eq. (6) describes the experimental data reasonably well, which allows it to be recommended for use in engineering calculations.

References

1. M. M. Dubinin, K. M. Nikolaev, and N. S. Polyakov, in *Uglerodnye adsorbenty i ikh primenenie v promyshlennosti* [*Carbon Adsorbents and Their Application in Industry*], Scientific Research Technological Institute of Carbon Sorbents, Perm', 1969, 97 (in Russian).

2. M. M. Dubinin, K. M. Nikolaev, N. S. Polyakov, and L. I. Petrova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 1265 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 1223 (Engl. Transl.)].

3. P. P. Zolotarev, M. M. Dubinin, K. M. Nikolaev, N. S. Polyakov, and L. V. Radushkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 1484 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21**, 1432 (Engl. Transl.)].

4. M. M. Dubinin, P. P. Zolotarev, K. M. Nikolaev, N. S. Polyakov, L. I. Petrova, and L. V. Radushkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 293 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22**, 279 (Engl. Transl.)].

5. K. M. Nikolaev, M. M. Dubinin, and N. S. Polyakov, in *Kinetika i dinamika fizicheskoi adsorbtsii* [*Kinetics and Dynamics of Physical Adsorption*], Ed. M. M. Dubinin, Nauka, Moscow, 1973, 117 (in Russian).

6. M. M. Dubinin, V. S. Kut'kov, A. V. Larin, K. M. Nikolaev, and N. S. Polyakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1235 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1111 (Engl. Transl.)].

7. V. S. Kut'kov, and N. S. Polyakov, in *Adsorbtsionnye protsessy v reshenii problem zashchity okruzhayushchey sredy* [*Adsorption Processes in the Solution of Environmental Problems*], Ed. A. E. Kreytus, Institute of Wood Chemistry of the Latv. AN, Riga, 1991, 8 (in Russian).

8. M. M. Dubinin, K. M. Nikolaev, N. S. Polyakov, and G. L. Pirozhkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1487 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1034 (Engl. Transl.)].

9. M. M. Dubinin, V. S. Kut'kov, K. M. Nikolaev, N. S. Polyakov, and A. V. Larin, *Zh. Fiz. Khim.*, 1982, **58**, 985 [*Sov. J. Phys. Chem.*, 1982, **58** (Engl. Transl.)].